Theoretical Estimation on the Balance Between the Absorption Coefficient and Etching Resistance of Various Polymers at 13 nm

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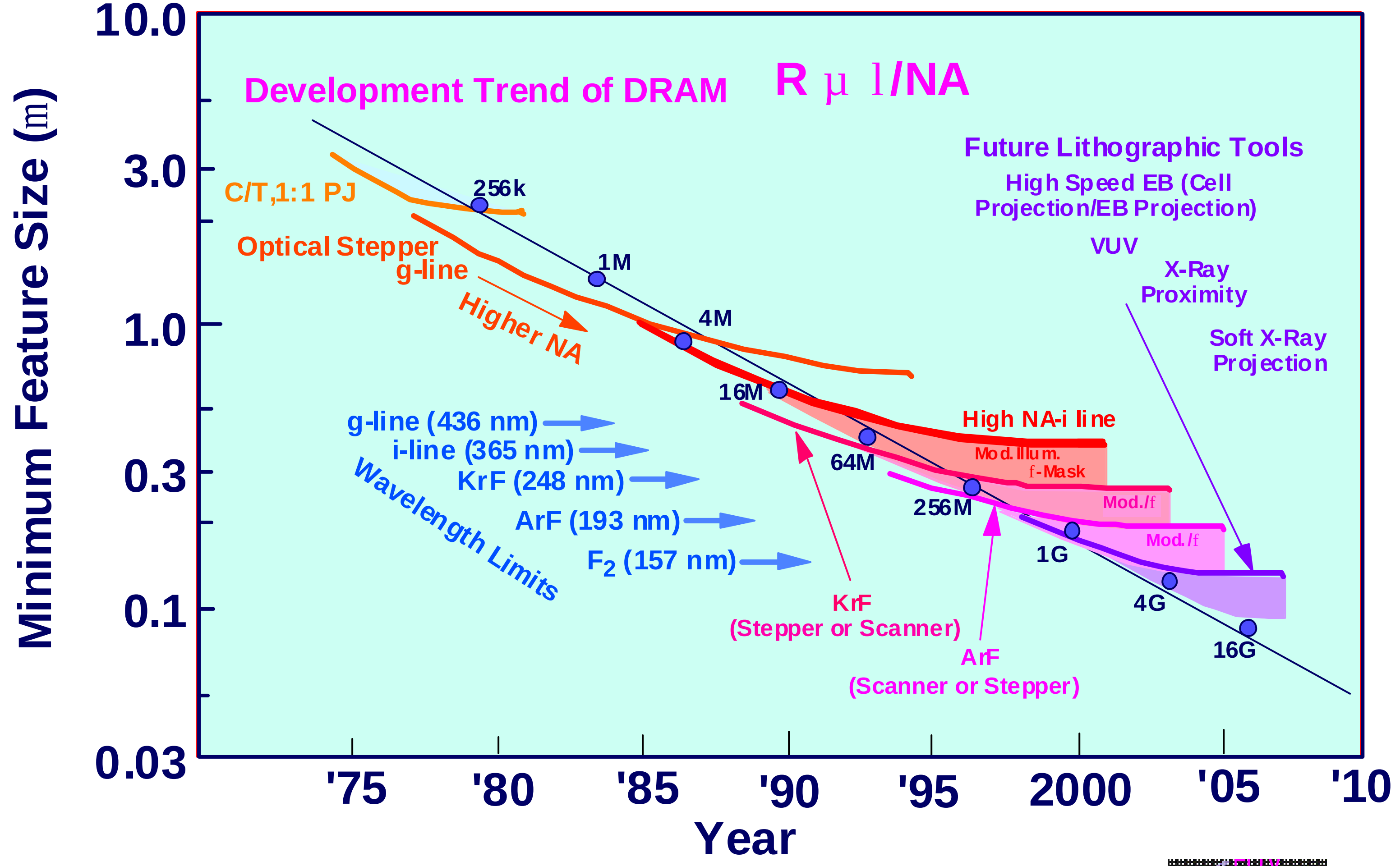
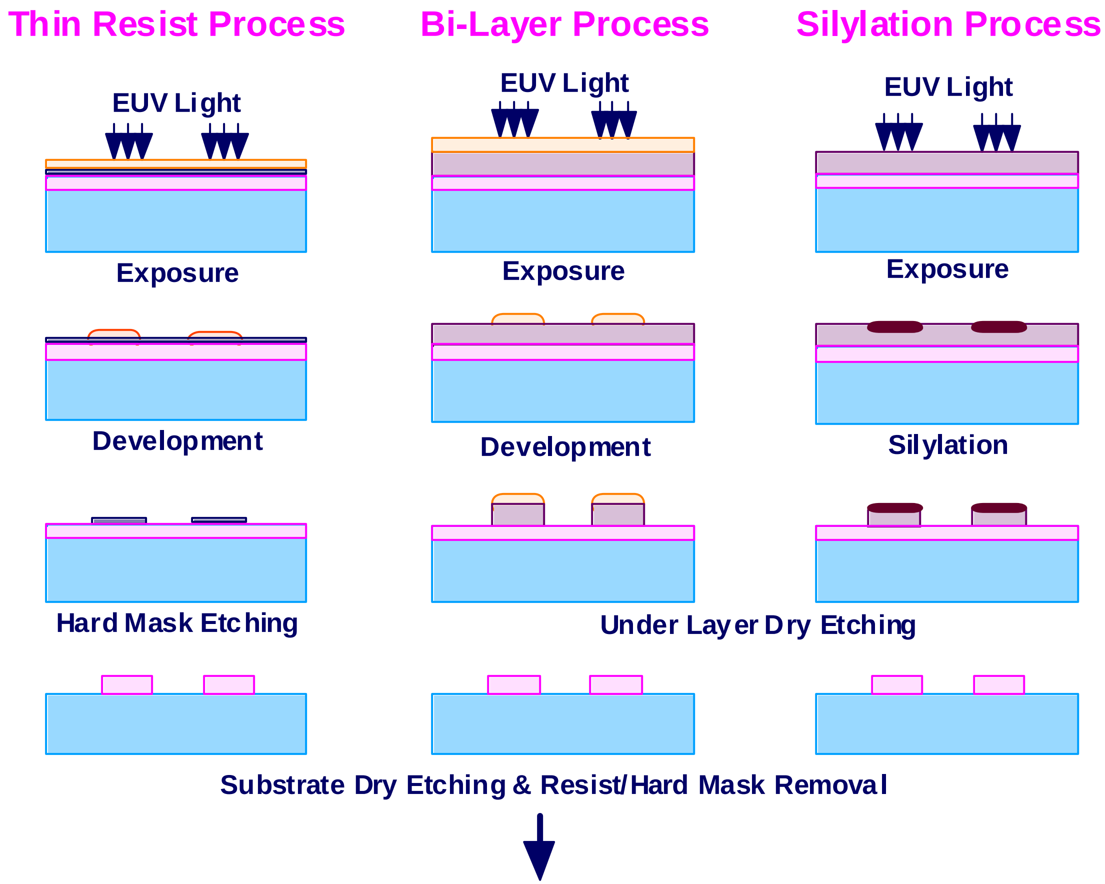
(ASET)


Development Trend of DRAM
R µ l/NA
Minimum Feature Size (m)
10.0
3.0
1.0
0.3
0.1
0.03
'75
'80
'85
'90
'95
2000
'05
'10
Year
C/T,1:1 PJ
Optical Stepper
g-line
Higher NA
256k
1M
4M
16M
64M
256M
1G
4G
16G
g-line (436 nm)
i-line (365 nm)
KrF (248 nm)
ArF (193 nm)
F2 (157 nm)
Wavelength Limits
High NA-i line
Mod.Illum.
Mod./f
Mod./f
KrF
(Stepper or Scanner)
ArF
(Scanner or Stepper)
Future Lithographic Tools
High Speed EB (Cell
Projection/EB Projection)
VUV
X-Ray
Proximity
Soft X-Ray
Projection

Introduction 2. Resist Processes for EUV Lithography



Absorption of polymers at 13nm is an important factor for molecular design

Introduction 3. Previous Study (G. D. Kubaik et al. JVST B 1992, 10, 2593)

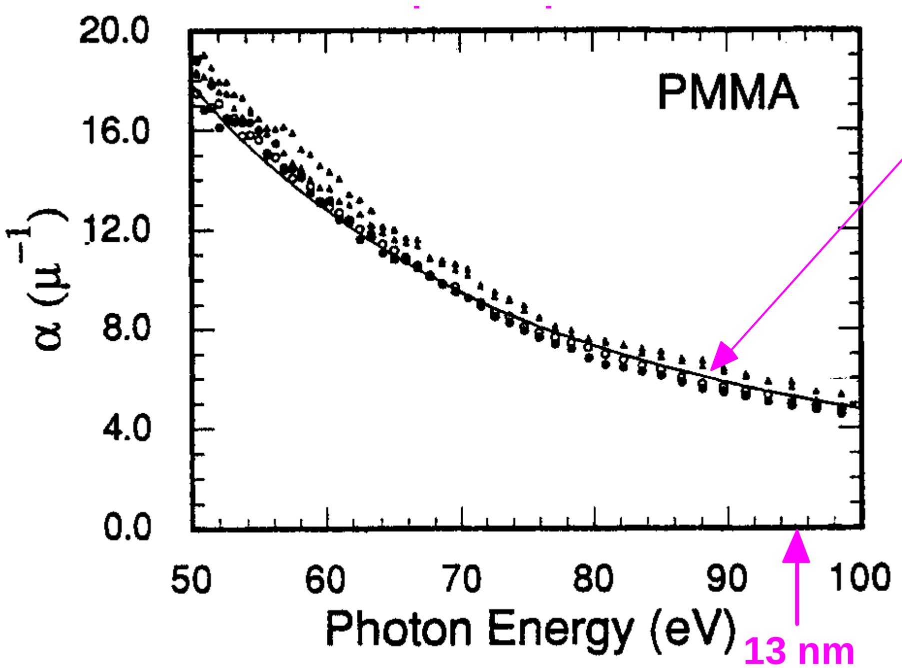


FIG. 3. Plot of the linear absorption coefficient vs photon energy of PMMA films determined from transmittance measurements made for four film thicknesses (Δ: 75 nm; ▲: 150 nm; ○: 163 nm; and ●: 220 nm). Solid curve is calculated from mass absorption coefficients and measured film density.

Calculated EUV Absorption Spectrum Using an Experimental Value of Density

$$\Sigma \mu_l = \Sigma \mu_a \times (N_o \rho / A)$$

μ_l: linear absorption coefficient

μ_a: mass absorption coefficient

→ Henke's Table

N_o: Avogadro's number

A: atomic weight

ρ: density of polymer

Introduction 4. Relative Atomic Absorption from Henke's Table

H:	1
C:	23.8
N:	49.6
O:	93.4
F:	141
Si:	13.6

H < Si < C < N < O < F

The Aim of This Work

- We would like to predict the absorption quicker than doing measurements

- Often, there are no experimental density available for resist polymers

↓

Prediction of density of polymers

↓

Prediction of the absorption

↓

Molecular Design of Resist Polymers

Calculation 1. Comparison to the Experiment

- Mass Absorption Coefficient by Henke et al.

B. L. Henke, E. M. Gullikson and J. C. Davis, *Atomic Data and Nuclear Data Tables*, 54 (1993) 181.

- Polymer Density Calculated by Using the Graph-Theoretical Treatment Derived by Bicerano et al. Implemented in the Program system "POLYMER".

J. Bicerano, *Predictions of the Properties of Polymers from their Structures*, Marcel Dekker: New York, 1993.

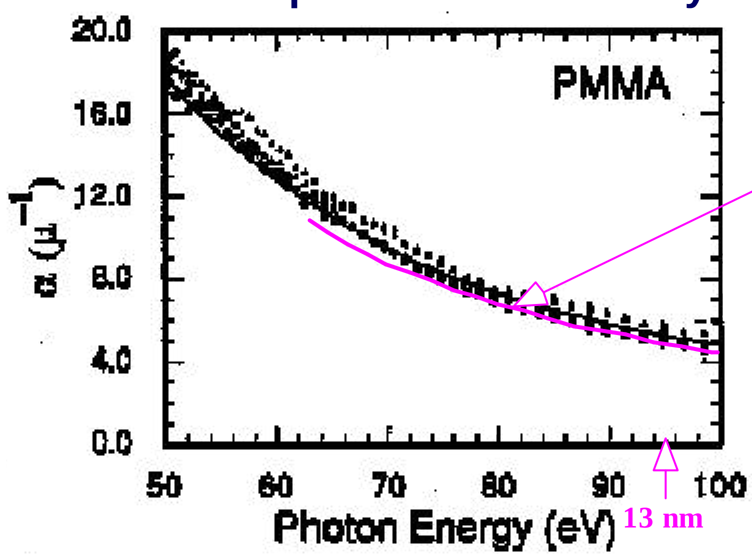
L. B. Kier and L. H. Hall, *Molecular Connectivity in Chemistry and Drug Research*, Academic Press: New York 1976.

L. B. Kier and L. H. Hall, *Molecular Connectivity in Structure-Activity Analysis*, John-Wiley & Sons: New York (1986).

The "POLYMER" program is available from MSI Inc., San Diego, CA.

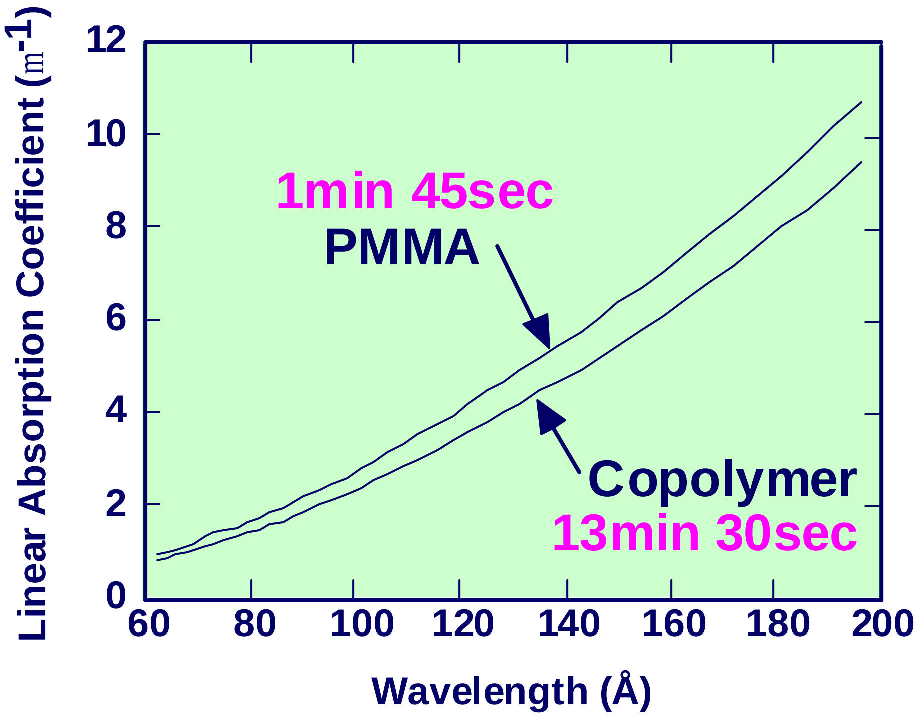
Accuracy of density prediction: Average error: 2.2 %

- Comparision to the Experimental Result by G. D. Kubaik et al.



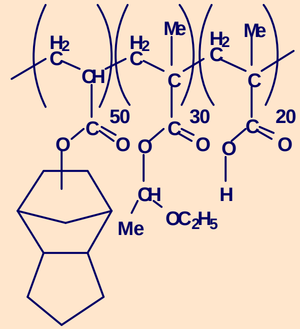
Our Calculated Result from the Calculated Density

Calculation 2. Computational Time Required



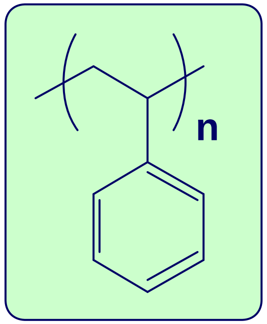
Note: The time shown includes time to make the input deck for computation

NEC Copolymer reported by Hasegawa et al.

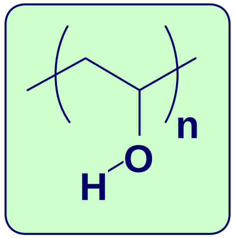


Ref: Nakano et al. Proc. SPIE 1994, 2195, 194; ibid 1995, 2438, 322

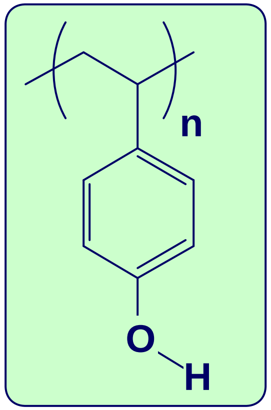
Results 1. Results on Some General Polymers



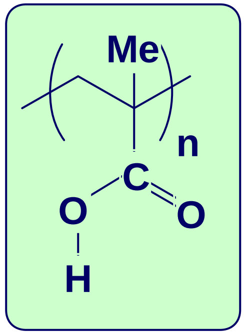
2.79 /m
43.3 %
75.7 %



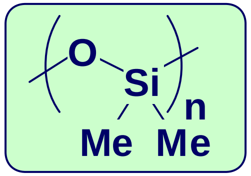
5.27 /m
20.6 %
59.0 %



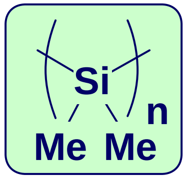
3.80 /m
32.0 %
68.4 %



5.38 /m
19.9 %
58.4 %



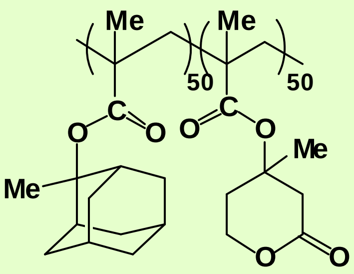
2.68 /m
44.8 %
76.5 %



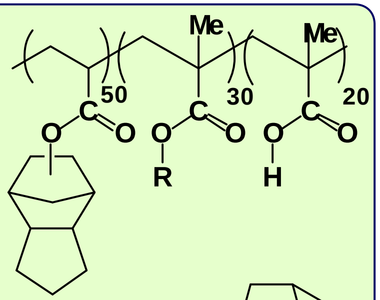
1.25 /m
68.8 %
88.3 %

linear abs coeff.
T @ 3000 Å
T @ 1000 Å

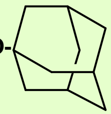
Results 2. Results on Some Reported Resist Polymers



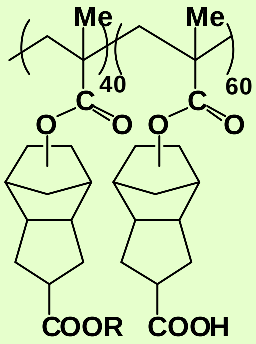
4.19 m^{-1}
28.5 %
65.8 %



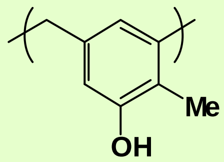
R = -CHMeOC $_2$H$_4$OCO-



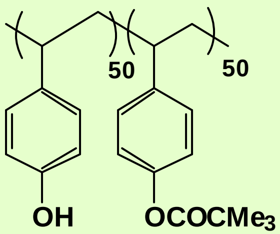
4.12 m^{-1}



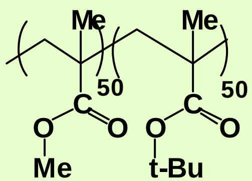
R=CHMeOEt

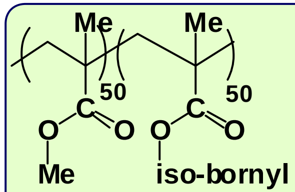


3.71 m^{-1}
32.9 %
69.0 %



3.95 m^{-1}
30.6 %
67.4 %





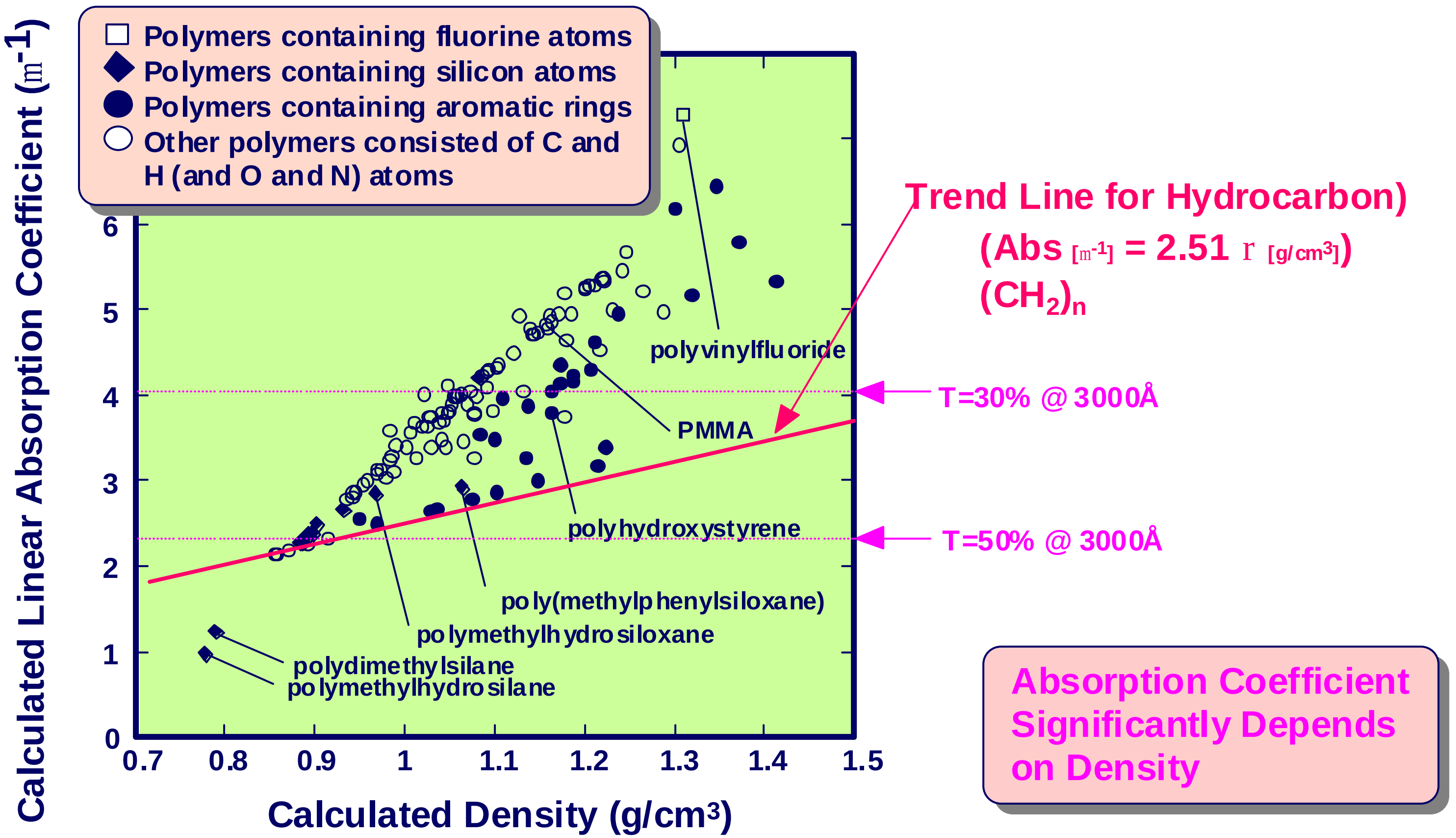
Results 3. Calculated Polymers

More than 140 polymers were calculated

acrylates, methacrylates, polyalkanes, polyvinylalcohol, polyvinylphenols, fluorinated polymers, silanes, siloxanes .....

polyacenaphthylene, polyacetal, polyacrylamide, polyacrylic acid, polyacrylonitrile, polybenzyl-acrylate, polybenzylmethacrylate, polybutadiene, poly(1-butene), poly(2-butoxyethyl acrylate), poly(n-butyl acrylate), poly(t-butyl acrylate), poly(t-butylaminoethylmethacrylate), poly(n-butyl methacrylate), poly(sec-butyl methacrylate), poly(t-butyl methacrylate), poly(1,4-butylene adipate), poly(1,4-butylene terephthalate), poly (t-butyl styrene), polycaprolactone, poly-carbonate, poly(cylcohexyl acrylate), poly (cylcohexyl methacrylate), poly(n-decyl acrylate), poly(n-decyl methacrylate), poly(di-t-butyl vinylpiridine), poly(2,6-dimethyl-1,4-phenylene oxide), poly(2,2-dimethyl-1,3-propylene succinate), poly(dimethylaminoethyl methacrylate), poly(2,3-dihydrofuran), poly-diethoxysiloxane, polydiethylsiloxane, poly-dimethylsiloxane, polydimethylsilane, poly(4,4'-dipropoxy-2,2'-diphenylpropane fumarate), poly(2-(2-ethoxyethoxy)-ethyl acrylate), poly (ethyl acrylate), poly(ethyl methacrylate), polyethylene, poly(ethylene adipate), poly (ethylene azelate), poly(ethylene glycol), poly (ethylene succinate), poly(ethylene terephthalate), poly(2-ethylhexyl acrylate), poly(2-ethylhexyl methacrylate), poly(ethyl methacrylate), poly-(hexadecyl methacrylate), poly(hexafluoro-propylene oxide), poly(hexamethylene sabacate), poly(n-hexyl acrylate), poly(n-hexyl methacrylate), poly(p-hydroxy benzoate), poly (hydroxybutyric acid), poly(4-hydroxybutyl-acrylate), poly(2-hydroxybutylacrylate), poly(2-hydroxyethylmethacrylate), poly(2-hydroxy-propylacrylate), poly(2-hydroxypropyl-methacrylate), poly(4-hydroxystyrene), poly-imide, poly(isobornyl-acrylate), poly(isobornyl-methacrylate), poly (isobutyl acrylate), poly-isobutylene, poly (isobutyl methacrylate), poly-isoprene, poly(isopropyl acrylate), poly (isopropyl methacrylate), poly(lauryl acrylate), poly(lauryl methacrylate), polymethacrylamide, poly(methacryl acid), polymethacrylonitrile, poly (2-methoxyethy acrylate), poly(4-methoxy-styrene), poly(methyl acrylate), poly(methyl methacrylate), poly(methylhexadexylsiloxane), poly(methyl-hexylsiloxane), poly(methylhydro-silane), poly(methylhydrosiloxane), poly (methyloctadexylsiloxane), poly(methyloctyl-siloxane), poly(methylphenylsiloxane), poly(4-methyl-1-pentene), poly(a-methylstyrene), poly (4-methylstyrene), poly(methyltetradecyl-siloxane), poly(neopentylmethacrylate), poly (neopentyl glycol sebacate), poly(octadecyl acrylate), poly(octadecyl methacrylate), poly (octyl_acrylate), poly(octyl_methacrylate), poly (2-phenoxyethyl acrylate), poly(2-phenoxyethyl methacrylate), poly(2-phenyl methacrylate), poly (phenylethyl methacrylate), poly(propyl methacrylate), poly(propyl acrylate), poly (propylene), poly(propylene glycol), polystyrene, polytetrafluoroethylene, polytetrahydrofuran, poly(tetrahydrofurfuryl methacrylate), poly (tetrahydrofurfuryl acrylate), poly(tridecyl methacrylate), poly(trimethylene adipate), poly (trimethylene glutarate), poly(trimethylene succinate), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl biphenyl), poly(vinyl carbazole), poly(vinyl cinnamate), poly(vinyl ethylether), poly(vinyl fluoride), poly(vinylidene fluoride), poly(vinyl laurate), poly(vinyl methylether), poly(vinyl methylketone), poly(vinyl naphthalene), poly(vinyl pivalate), poly(vinyl propionate), poly(2-vinyl piridine), poly(vinyl stearate), Nylon-6, Nylon-6/6, Nylon-6/9, Nylon-6/10, Nylon-6/12, Nylon-11, Nylon-12

Results 4. Calculated Linear Absorption Coefficient at 13 nm for Various Polymers

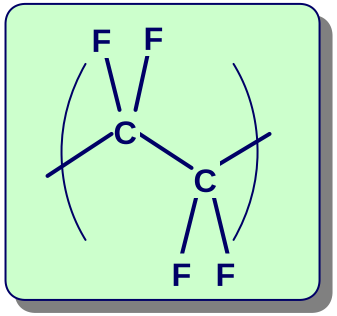


Absorption Coefficient Significantly Depends on Density

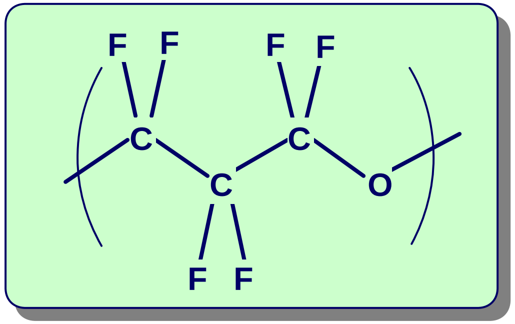
Results 5.

Results on Fluorinated Polymers

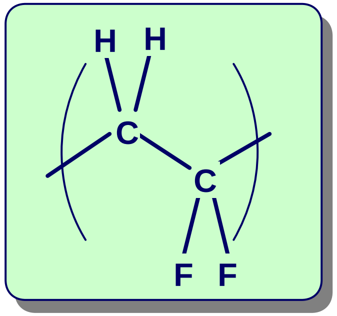
Density
Linear Absorption
T @ 1000 Å



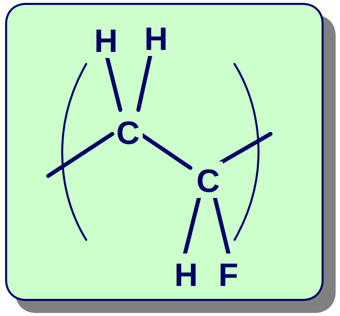
2.053 g/cm^3
16.4 /m
0.7 %



2.022 g/cm^3
16.1 /m
0.8 %



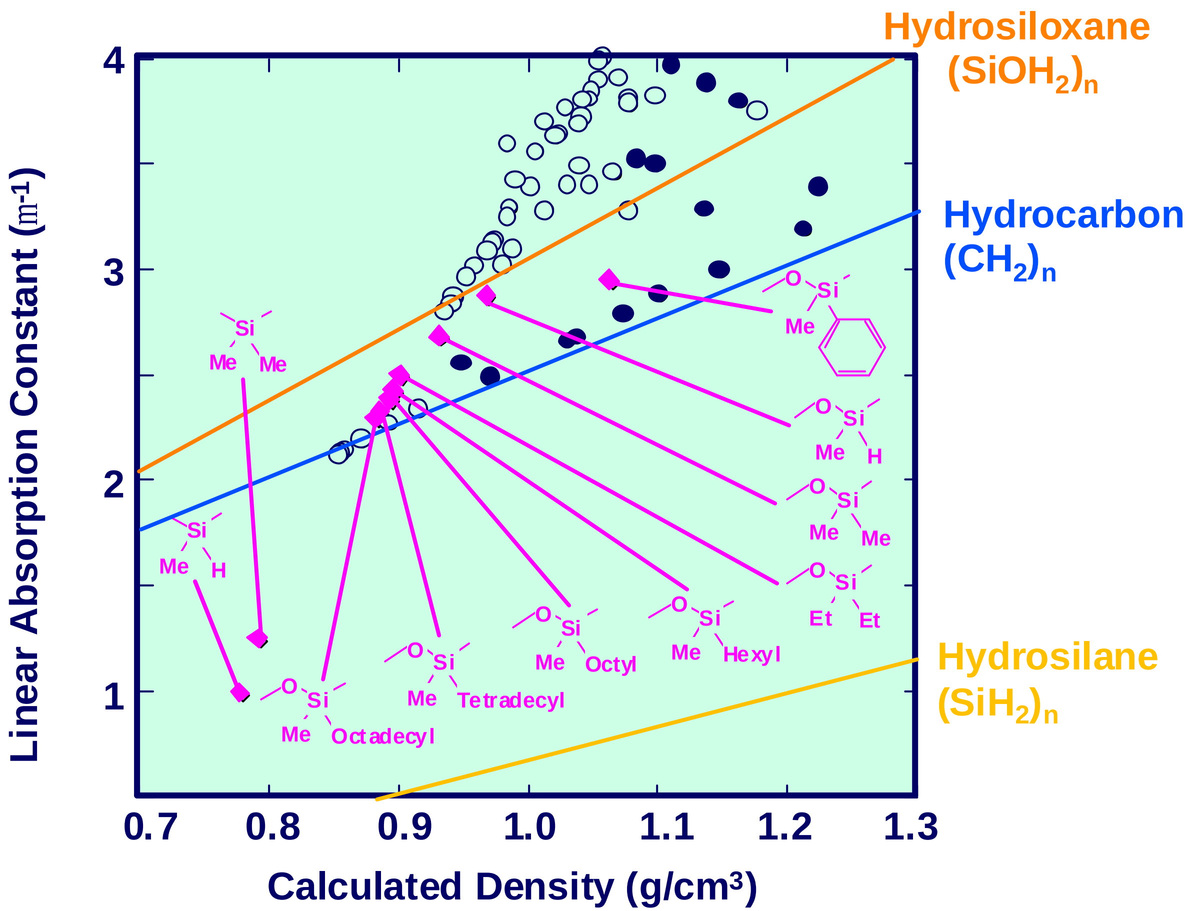
1.606 g/cm^3
11.0 /m
3.7 %



1.310 g/cm^3
7.3 /m
11.2 %

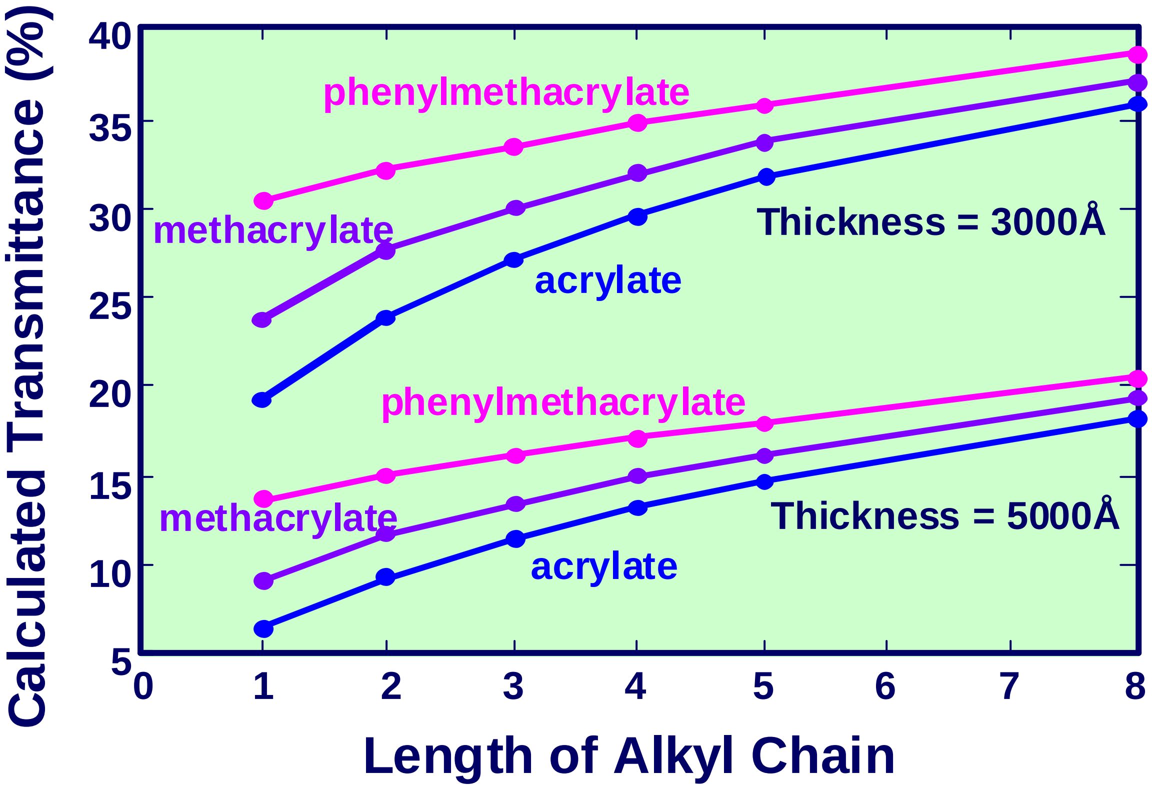
Values for fluorinated polymers are too large

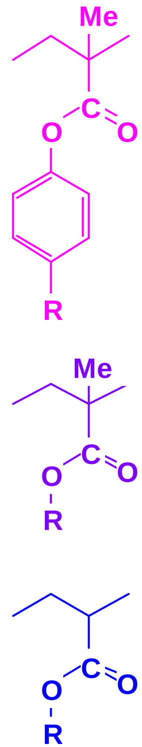
Results 6. Silicon Containing Polymers



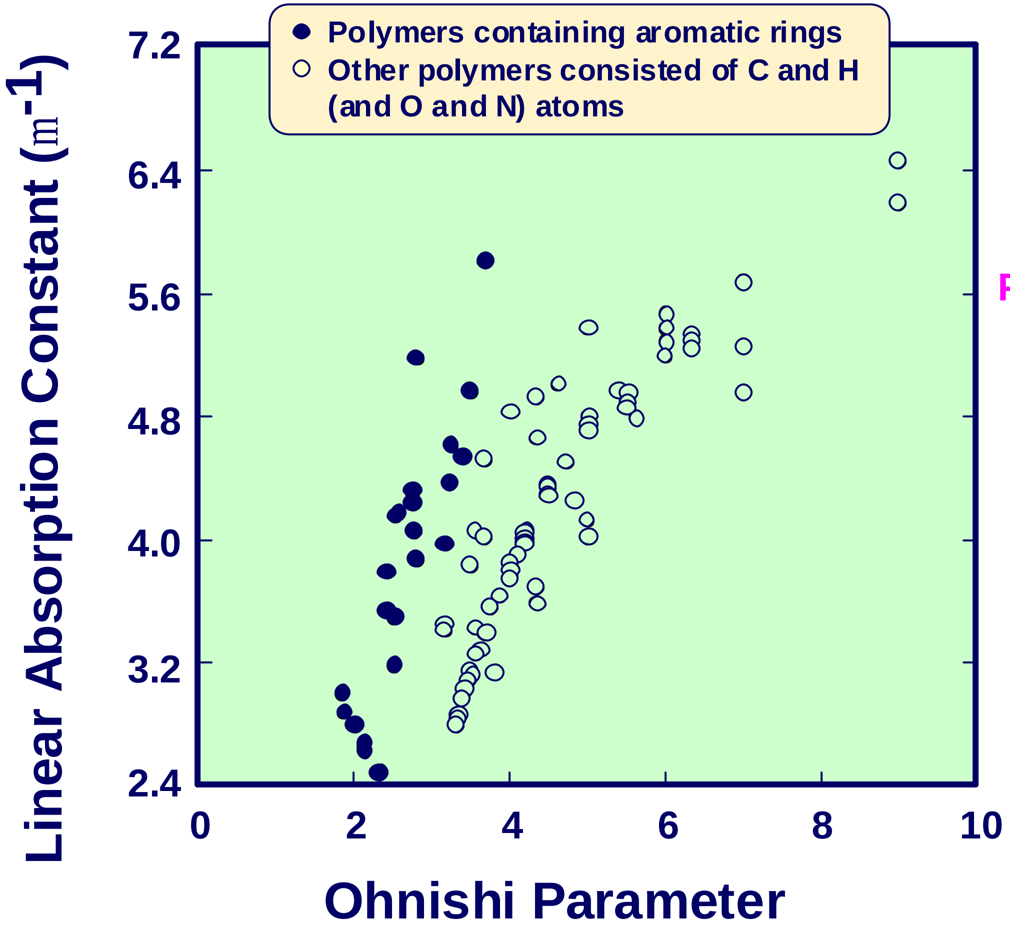
Results 7.

Effect of the Addition of a Phenyl Ring or the Elongation of Alkyl Chain





Results 8.



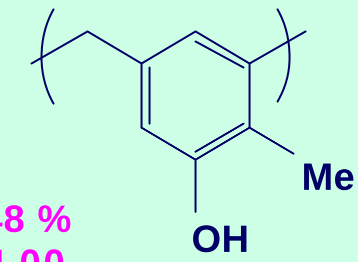
Phenyl Substitution leads to
Lower Absorption and
Higer Etching Resistance

↓

Single Layer Resist Process?

Results 9.

T (@200nm)
Normalized Ohnishi Param.



48 %
1.00

Sorry!!
Chemical Structures
cannot be shown
because of the IP issue

48 %
0.86

Sorry!!
Chemical Structures
cannot be shown
because of the IP issue

48 %
0.79

Sorry!!
Chemical Structures
cannot be shown
because of the IP issue

53 %
0.96

Further designing of novel polymers for EUVL are now in progress!!